

Theory and Practice of Density Functional Theory

Peter E. Blöchl
Institute for Theoretical Physics
Clausthal University of Technology, Germany

<http://www.pt.tu-clausthal.de/atp/>



Standard model of Solid State Physics

- particles: nuclei and electrons
- interaction: **electrostatics**
- equations of motion:

– Schrödinger equation: $i\hbar\partial_t|\Psi\rangle = \hat{H}|\Psi\rangle$

– Poisson equation: $\nabla^2\Phi(\vec{r}) = \frac{1}{\epsilon_0}\rho(\vec{r})$

but:

exponential wall of many-particle physics

problem:

quantum mechanics + interaction

Density functional theory

maps **interacting electrons** onto **non-interacting quasi-electrons** in an **effective potential**

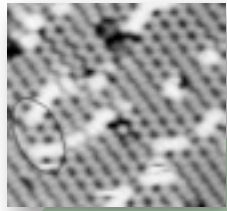
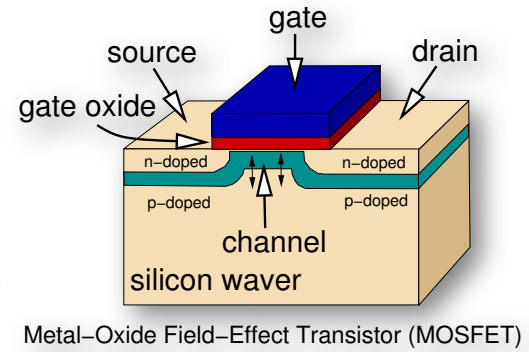
- one-particle Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \vec{\nabla}^2 + v_{eff}(\vec{r}) \right) \psi_n(\vec{r}) = \psi_n(\vec{r}) \epsilon_n$$

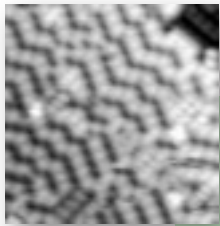
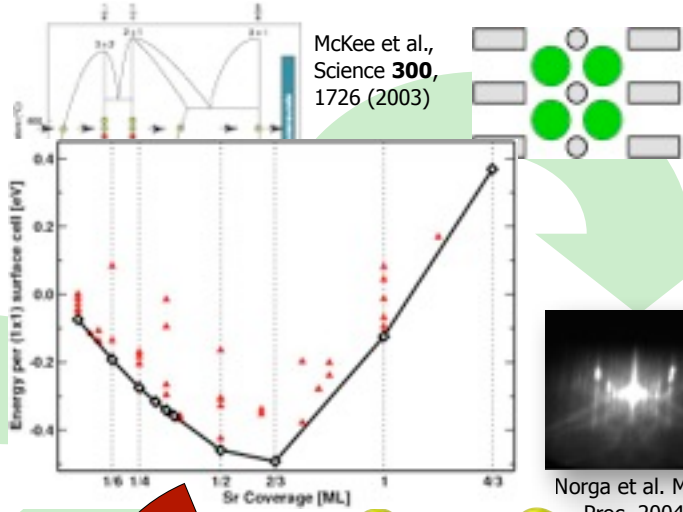
- limited to ground state properties
- based on an exact theorem
 - but: implementation requires approximations

Appetizer: high-K oxides for new transistors

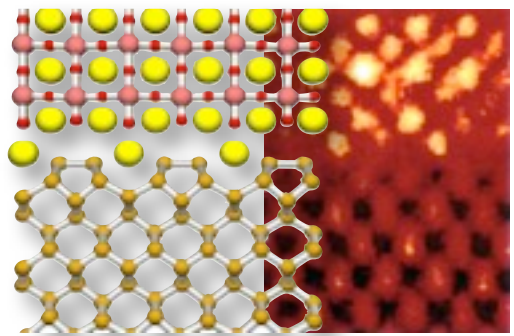
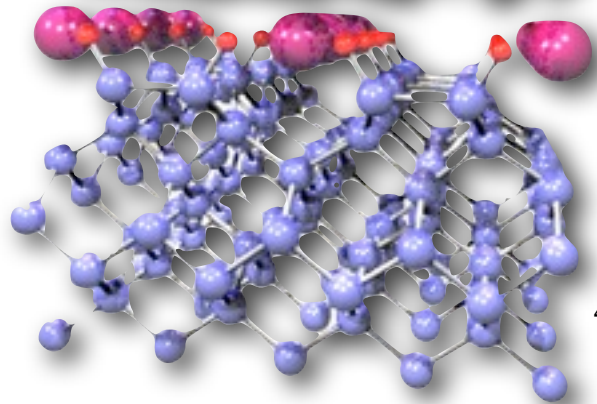
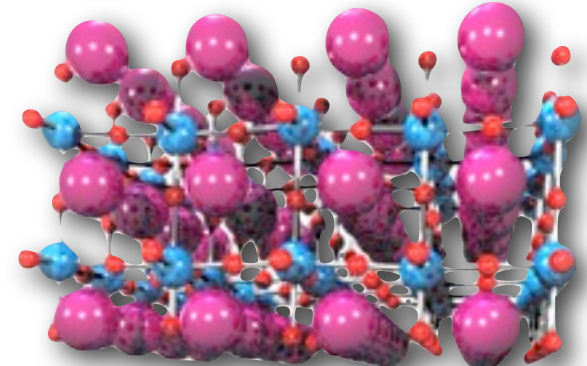
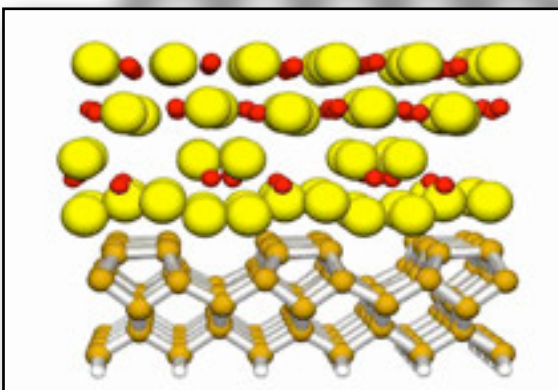
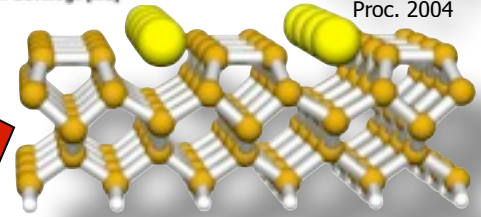
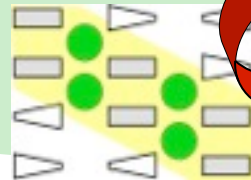
Först, Ashman, Schwarz, Blöchl, Nature 53, 427 (2004)
Ashman, Först, Schwarz, Blöchl, PRB 69, 75309 (2004)
Först, Ashman, Blöchl, German patent DE10303875



Hu et al.
PRB65,75408(2002)



Ojima, Yoshimura, Ueda
PRB65, 75408 (2004)



Total energy functional

- Minimize total energy functional:

$$\begin{aligned}
 E[|\psi_n\rangle, f_n] &= \underbrace{\sum_n f_n \langle \psi_n | \frac{\hat{p}^2}{2m} | \psi_n \rangle}_{E_{kin}} + \underbrace{\frac{1}{2} \int d^3r \int d^3r' \frac{e^2 [n(\vec{r}) + Z(\vec{r})][n(\vec{r}') + Z(\vec{r}')] }{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}}_{E_{Hartree}} \\
 &+ \underbrace{E_{xc}[n(\vec{r})]}_{E_{xc}} - \sum_{n,m} \Lambda_{n,m} \underbrace{(\langle \psi_n | \psi_m \rangle - \delta_{n,m})}_{\text{constraint}} \\
 \text{with} \quad n(\vec{r}) &= \underbrace{\sum_n f_n |\psi(\vec{r})|^2}_{\text{electron density}} \quad Z(\vec{r}) = - \underbrace{\sum_j Z_j \delta(\vec{r} - \vec{R}_j)}_{\text{charge density of nuclei in electron charges}}
 \end{aligned}$$

- Solve Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 + v_{eff}(\vec{r}) \right] \psi_n(\vec{r}) = \psi_n(\vec{r}) \epsilon_n \quad \text{and} \quad v_{eff}(\vec{r}) = \underbrace{\int d^3r' \frac{e^2 [n(\vec{r}') + Z(\vec{r}')] }{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}}_{v_{Hartree}(\vec{r})} + \underbrace{\frac{\delta E_{xc}}{\delta n(\vec{r})}}_{\mu_{xc}(\vec{r})}$$

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with

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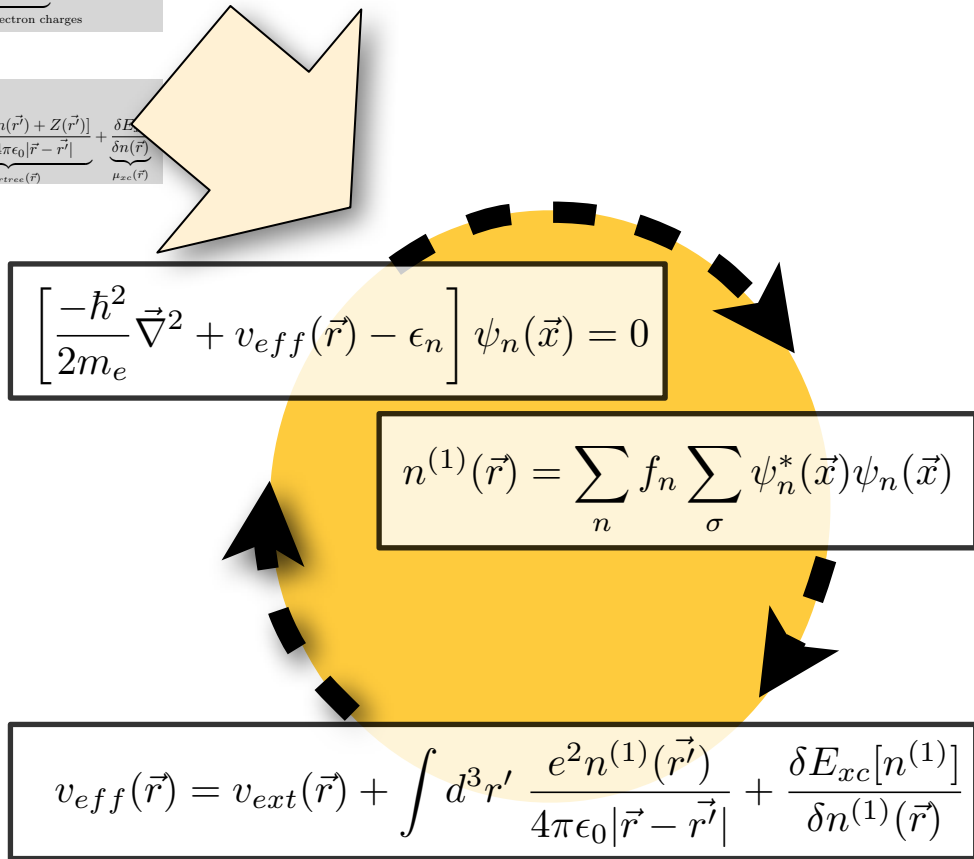
Self-consistency loop

$$E[\psi_n, f_n] = \underbrace{\sum_n f_n \langle \psi_n | \frac{\hat{p}^2}{2m} | \psi_n \rangle}_{E_{kin}} + \underbrace{\frac{1}{2} \int d^3r \int d^3r' \frac{e^2 [n(\vec{r}) + Z(\vec{r})][n(\vec{r}') + Z(\vec{r}')] }{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}}_{E_{Hartree}}$$

$$+ \underbrace{E_{xc}[n(\vec{r})]}_{E_{xc}} - \underbrace{\sum_{n,m} \Lambda_{n,m} (\langle \psi_n | \psi_m \rangle - \delta_{n,m})}_{\text{constraint}}$$

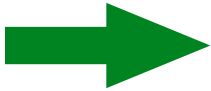
with $n(\vec{r}) = \underbrace{\sum_n f_n |\psi(\vec{r})|^2}_{\text{electron density}}$ $Z(\vec{r}) = - \underbrace{\sum_j Z_j \delta(\vec{r} - \vec{R}_j)}_{\text{charge density of nuclei in electron charges}}$

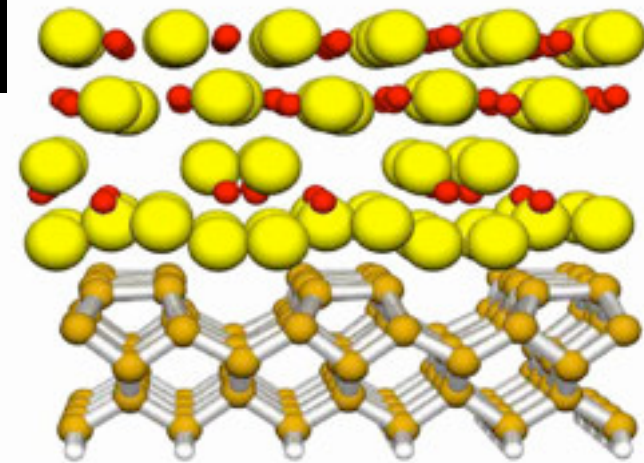
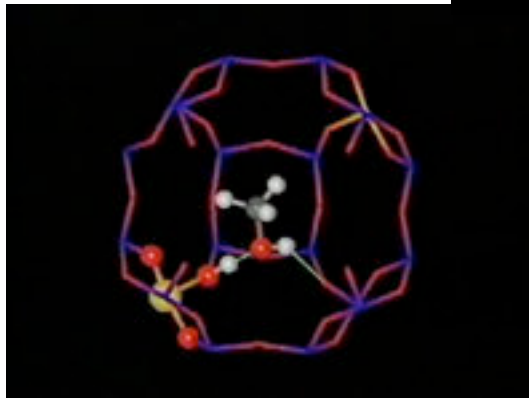
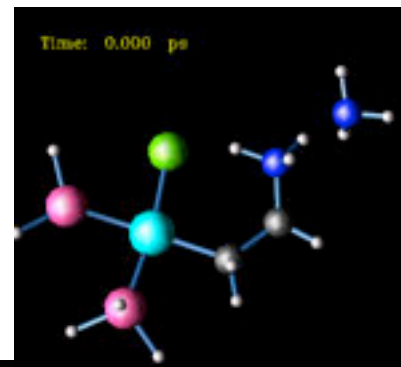
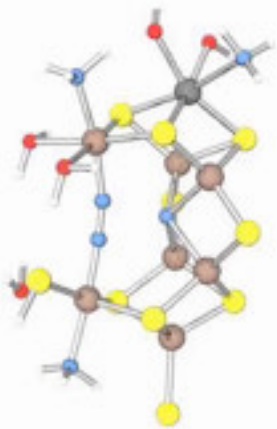
$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\vec{r}) \right] \psi_n(\vec{r}) = \psi_n(\vec{r}) \epsilon_n \quad \text{and} \quad v_{eff}(\vec{r}) = \underbrace{\int d^3r' \frac{e^2 [n(\vec{r}') + Z(\vec{r}')] }{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}}_{v_{Hartree}(\vec{r})} + \underbrace{\frac{\delta E}{\delta n(\vec{r})}}_{\mu_{xc}(\vec{r})}$$



Car-Parrinello method

Car, Parrinello, PRL 55, 2471(1985)

- Paradigm shift:
 - ~~eigenvalue problems~~  minimize energy
- Access to the molecular dynamics



Levy's constrained search

Is there a density functional?

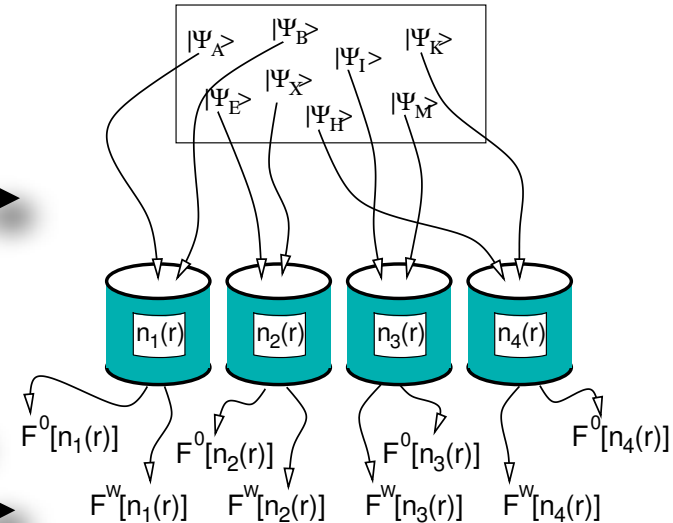
constrained search:

proof of existence by presenting a construction principle

1. sort all fermionic many-particle wave functions according to their density
2. For each density find
 - a. the wave function with lowest kinetic energy and
 - b. the wave function with lowest kinetic and interaction energy

This defines two universal density functionals, $F^0[n]$ and $F^W[n]$

3. determine energy and density of the ground state for a given external potential by minimization over all densities
 - potential energy depends only on the density



$$F^W[n] = \min_{|\Psi\rangle}^{\lambda^W(\vec{r}), E^W} \underbrace{\langle \Psi | \hat{T} + \hat{W} | \Psi \rangle}_{\text{kinetic + interaction}} + \int d^3r \lambda^W(\vec{r}) \underbrace{\left(\langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle - n(\vec{r}) \right)}_{\text{density constraint}} - E^W \underbrace{\left(\langle \Psi | \Psi \rangle - 1 \right)}_{\text{norm constraint}}$$

$$F^0[n] = \min_{|\Psi\rangle}^{\lambda^0(\vec{r}), E^0} \underbrace{\langle \Psi | \hat{T} | \Psi \rangle}_{\text{kinetic}} + \int d^3r \lambda^0(\vec{r}) \underbrace{\left(\langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle - n(\vec{r}) \right)}_{\text{density constraint}} - E^0 \underbrace{\left(\langle \Psi | \Psi \rangle - 1 \right)}_{\text{norm constraint}}$$

$$E_0 = \min_{n(\vec{r})}^{\mu} \left\{ F^W[n] + \int d^3r v_{ext}(\vec{r})n(\vec{r}) - \mu \underbrace{\left(\int d^3r n(\vec{r}) - N \right)}_{\text{charge constraint}} \right\}$$

$$= \min_{n(\vec{r})}^{\mu} \left\{ \underbrace{T_s[n]}_{F^0[n]} + \int d^3r v_{ext}(\vec{r})n(\vec{r}) + \underbrace{F^W[n] - F^0[n]}_{E_H + E_{xc}} - \mu \underbrace{\left(\int d^3r n(\vec{r}) - N \right)}_{\text{charge constraint}} \right\}$$

Exchange-correlation hole

- interaction energy

$$E_{e-e} = \frac{1}{2} \int d^3r \int d^3r' \frac{e^2 n^{(2)}(\vec{r}, \vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}$$

- two-particle density

- $n^{(2)}(r, r')$ = probability density of finding one electron at r and another at r' times $N(N-1)$ (number of pairs)

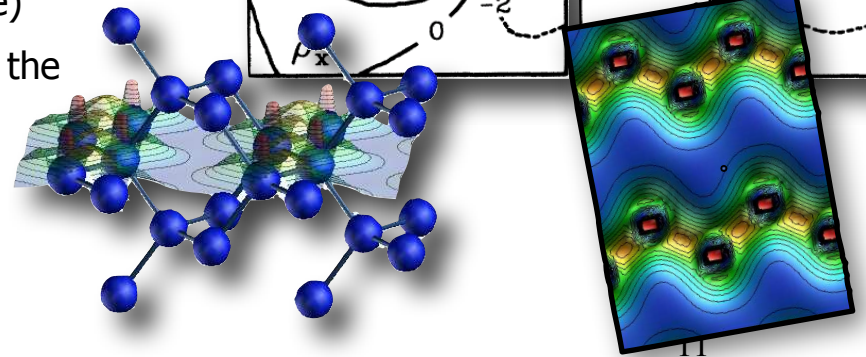
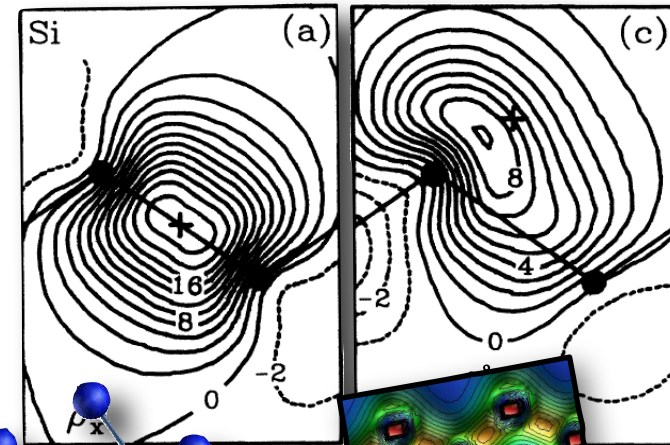
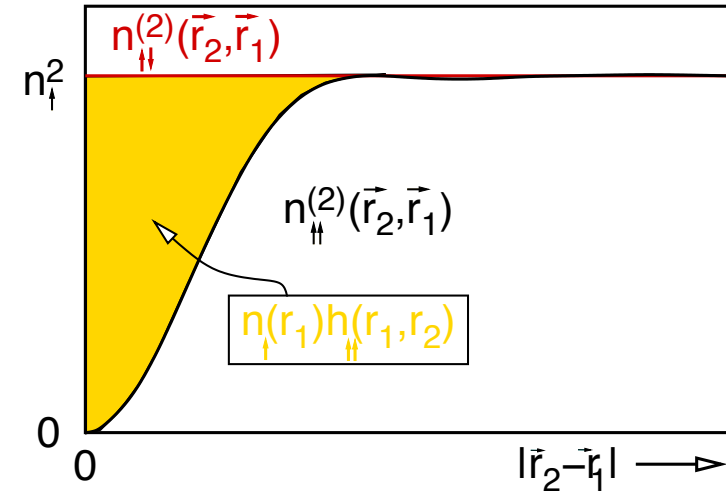
- exchange correlation hole $h_{xc}(r, r')$

$$n^{(2)}(\vec{r}, \vec{r}') = n^{(1)}(\vec{r})n^{(1)}(\vec{r}') + n^{(1)}(\vec{r})h_{xc}(\vec{r}', \vec{r})$$

$$E_{e-e} = \underbrace{\frac{1}{2} \int d^3r \int d^3r' \frac{e^2 n^{(1)}(\vec{r})n^{(1)}(\vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}}_{\text{Hartree energy}} + \underbrace{\int d^3r n^{(1)}(\vec{r}) \cdot \left[\frac{1}{2} \int d^3r' \frac{e^2 h_{xc}(\vec{r}', \vec{r})}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \right]}_{\text{potential energy of exchange and correlation}}$$

- properties of the exchange correlation hole

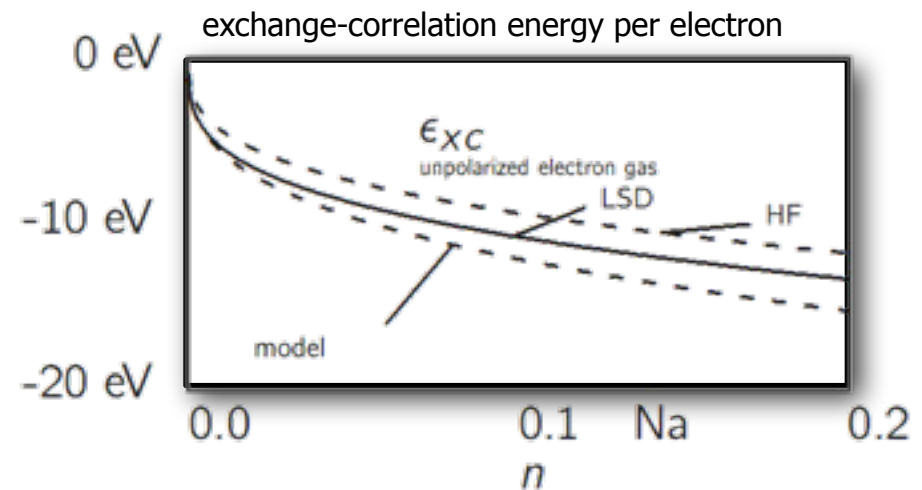
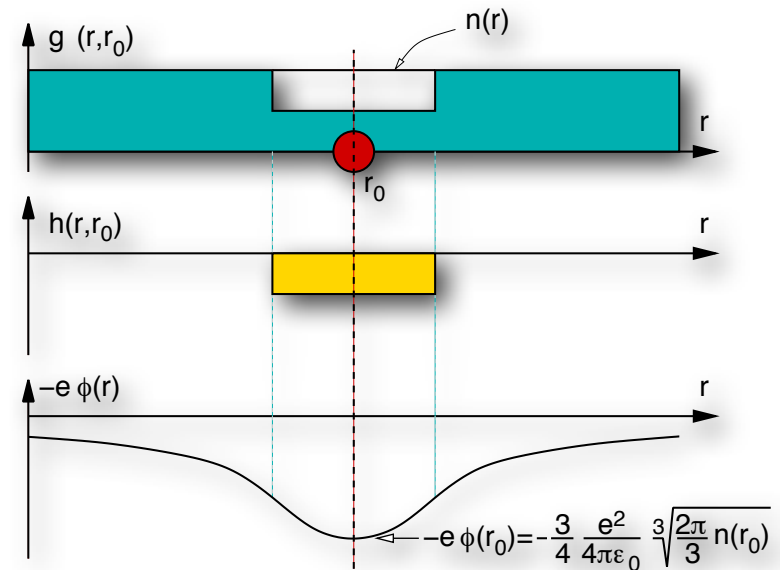
- each electron interacts with $N-1$ other electrons: hole integrates to -1 electron (Charge sum rule)
 - two electrons with the same spin cannot be at the same position (Pauli principle)
 - the hole vanishes at large distances (short-sightedness)



Model for E_{xc}

- properties of the exchange correlation hole
 - each electron interacts with N-1 other electrons: hole integrates to -1 electron (Charge sum rule)
 - two electrons with the same spin cannot be at the same position (Pauli principle)
 - the hole vanishes at large distances (short-sightedness)
- Model:
 - homogeneously charged sphere

For a free electron gas not much worse than a Hartree Fock calculation



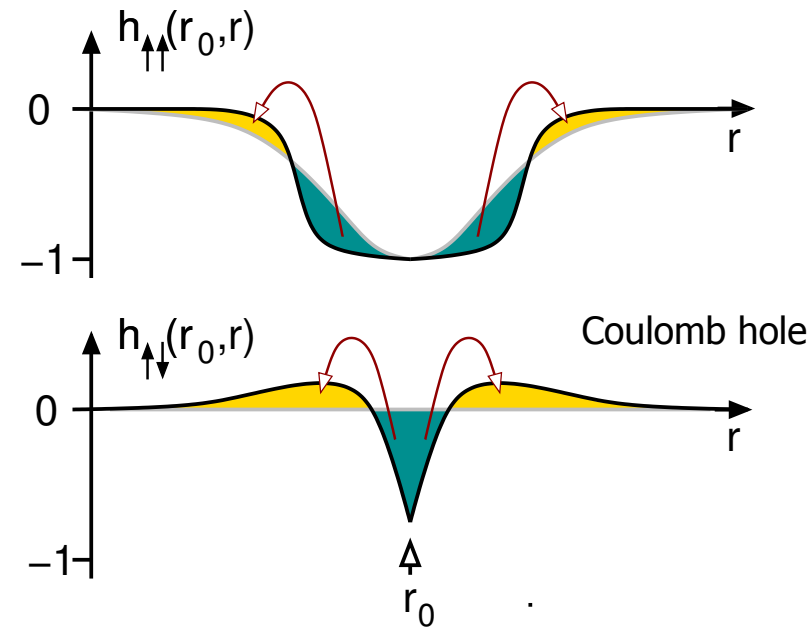
Correlation energy

$$E_{xc}[n^{(1)}] = F^W[n^{(1)}] - F^0[n^{(1)}] - E_{\text{Hartree}}$$

- Exchange energy uses hole of non-interacting electrons
- Coulomb repulsion pushes electrons away
- deformation of wave function raises kinetic energy

Correlation energy is due to the balance between energy gain by lowering the Coulomb repulsion and kinetic energy cost

- **adiabatic connection:**
 - switch the interaction slowly on and integrate opposing “force”
 - never evaluate kinetic energy explicitly



$$\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{W}$$

$$E_{xc} = \int_0^1 d\lambda \underbrace{\int d^3r n(\vec{r}) \frac{1}{2} \int d^3r' \frac{e^2 h_\lambda(\vec{r}, \vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}}_{dE/d\lambda}$$

$$= \int d^3r n(\vec{r}) \frac{1}{2} \int d^3r' \frac{e^2 \int_0^1 d\lambda h_\lambda(\vec{r}, \vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}$$

Jacobs ladder to heaven

5. **Exact:** Constrained search
4. **Hybrid functionals:** Include exact (nonlocal) exchange: left-right correlations
3. **Meta-GGA:** use kinetic energy density to estimate the flexibility of the electron gas
2. **GGA:** asymmetry of the xc-hole favors surfaces and thus weakens bonds
1. **LDA:** xc-hole from free electron gas: strong overbinding

Local density approximation (LDA)

- Local density approximation (LDA) imports the "exact" exchange correlation hole of a free electron gas

$$E_{xc} = \int d^3r n(\vec{r}) \epsilon_{xc}(n(\vec{r}))$$

local

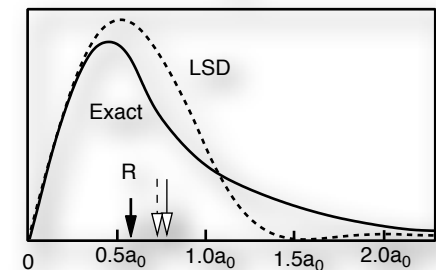
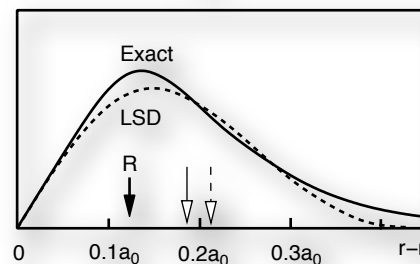
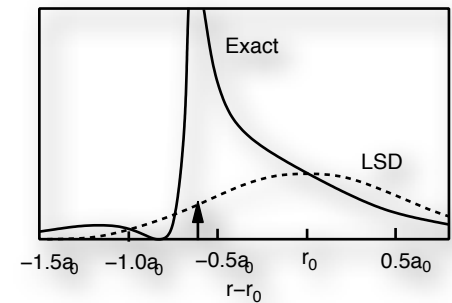
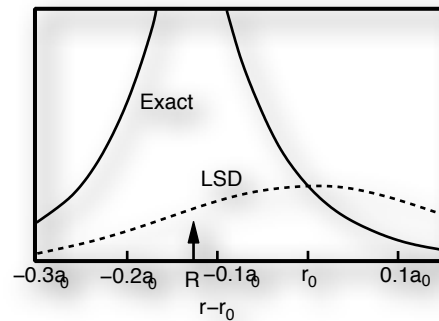
from free electron gas

Why does it work?
Sum rules!

$$\epsilon_{xc} = \frac{1}{2} \frac{4\pi e^2}{4\pi\epsilon_0} \int_0^\infty dr r \left\langle h(\vec{r}_0, \vec{r}_0 + \vec{r}) \right\rangle_{\text{angle}}$$

$$1 = 4\pi \int_0^\infty dr r^2 \left\langle h(\vec{r}_0, \vec{r}_0 + \vec{r}) \right\rangle_{\text{angle}}$$

- charge sum rule exact
- only spherical average matters
- only first moment of radial hole matters



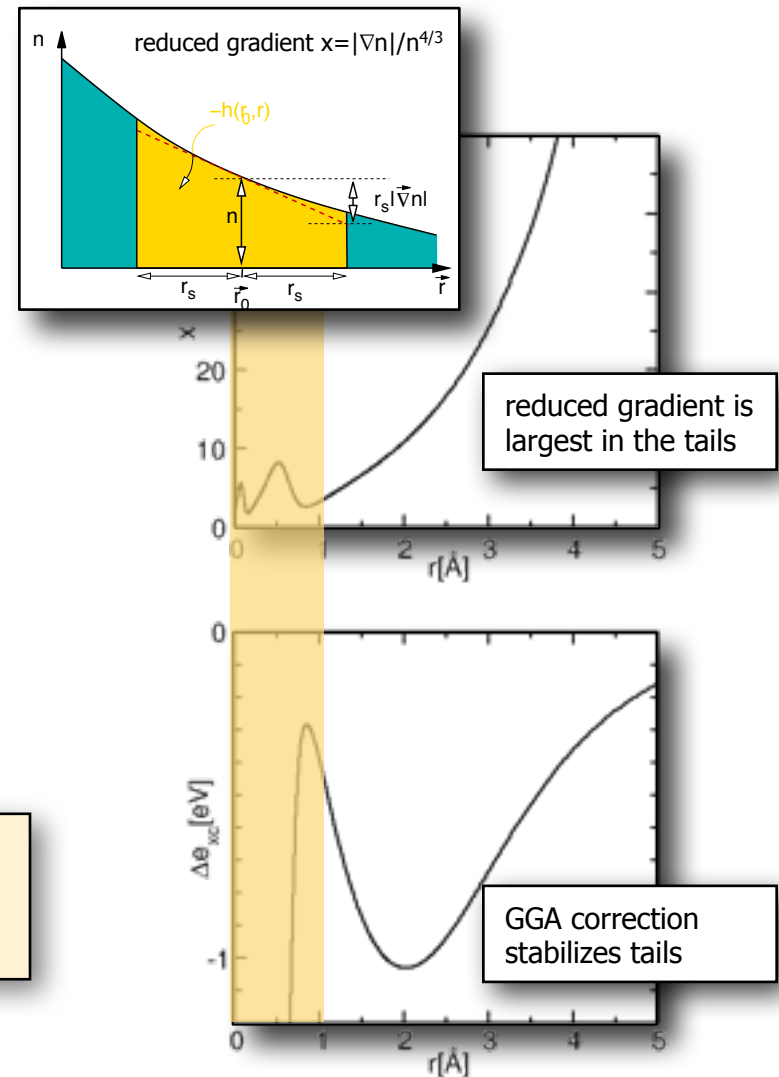
Generalized gradient approximation (GGA)

- an electron far away from an atom sees a positive ion
- the exchange hole is entirely on the atom.
- the LDA hole is centered on the electron and smeared out over a wide region.
- LDA overestimates the exchange energy at the surface

$$\epsilon_{xc}(r \rightarrow \infty) = \underbrace{-\frac{1}{2} \frac{e^2}{4\pi\epsilon}}_{GGA} r^{-1} \ll \underbrace{A \exp(-\lambda r)}_{LDA}$$

- GGA stabilizes the surfaces (overbinding reduced)

binding energies are dramatically improved
DFT became of interest to chemists



Hybrid functionals

- adiabatic connection

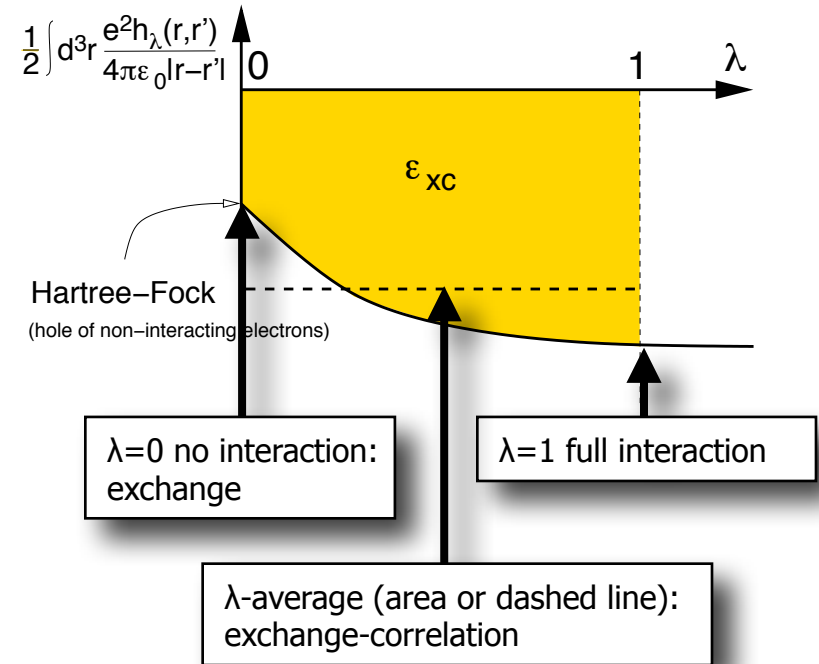
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- approximate integral by weighted sum of the values at the end-points of the interval

- Hartree-Fock exchange introduces nonlocality
- finite band gaps for Mott insulators
- correct dissociation limit of bonds
- related to GW, LDA+U, etc.



$$E_{xc} = \int d\lambda U_{xc}(\lambda)$$

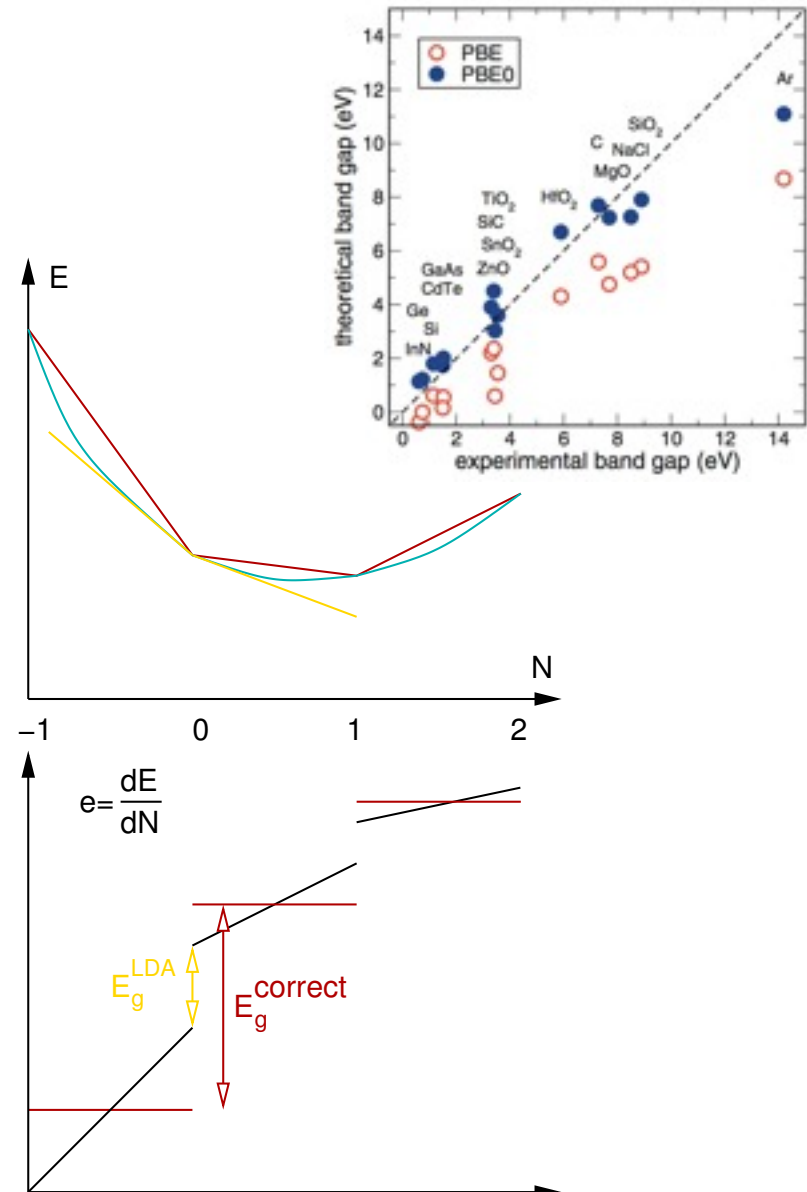
$$\approx \frac{1}{4} U_{xc}(\lambda=0) + \frac{3}{4} U_{xc}(\lambda=1)$$

$$= \frac{1}{4} \underbrace{U_{xc}^{HF}}_{E_x^{HF}} - \frac{1}{4} \underbrace{U_{xc}^{GGA}}_{E_x^{GGA}} + \frac{1}{4} \underbrace{U_{xc}^{GGA}(\lambda=0)}_{E_x^{GGA}} + \frac{3}{4} \underbrace{U_{xc}^{GGA}(\lambda=1)}_{E_x^{GGA}}$$

$$= E_{xc}^{GGA} + \frac{1}{4} (E_x^{HF} - E_x^{GGA})$$

Band-gap problem

- GGA's underestimate band gaps
 - in silicon 0.7 eV instead of 1.17 eV
- Many transition metal oxides are metals instead of insulators!
- Problem: energy of average density instead of average of energies



Electronic structure methods:

how to solve the Kohn-Sham equations

augmented wave methods

Korringa Kohn Rostocker (KKR), augmented plane wave (APW) method

pseudopotentials

Hamann-Bachelet-Schlueter, Troulier-Martins, Kleinman-Bylander, Vanderbilt ultrasoft

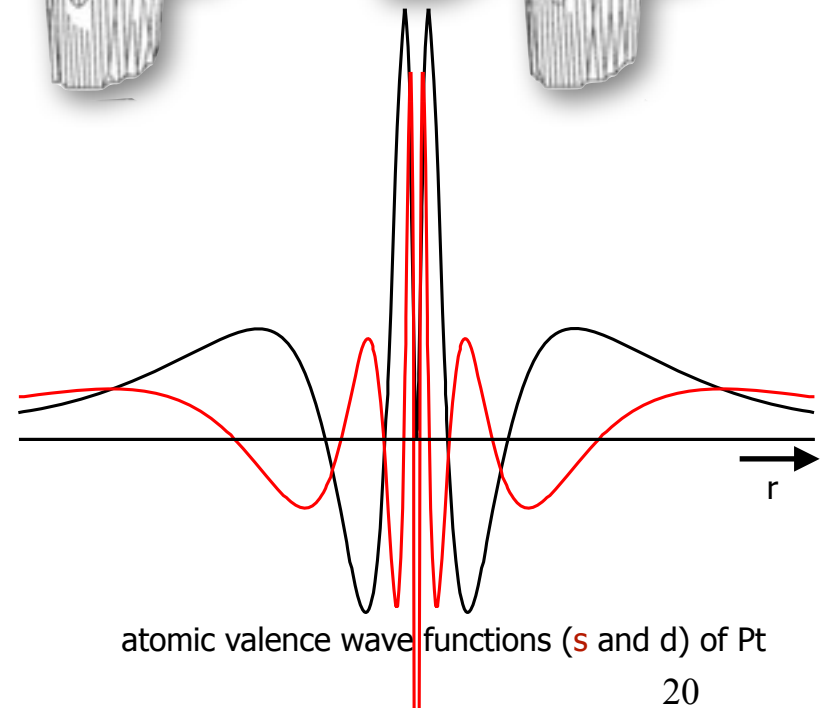
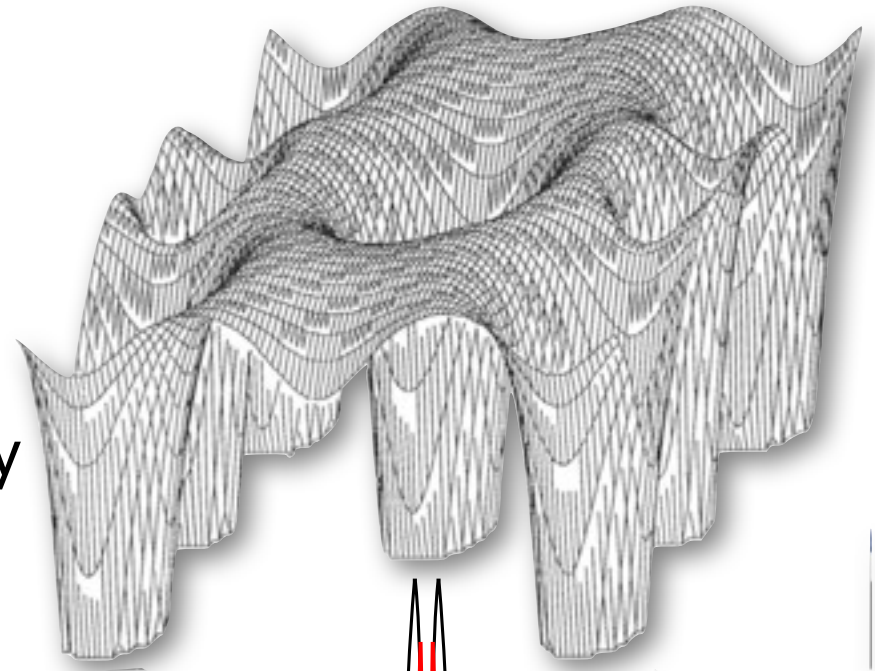
linear methods

linear augmented muffin tin-orbital (LMTO) method
linear augmented plane wave (LAPW) method

**projector augmented
wave method**

What is the problem?

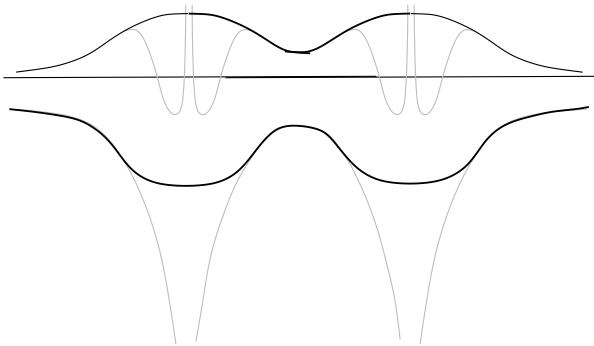
1. wave function oscillates strongly in the atomic region (Coulomb singularity)
2. wave function needs to be very flexible in the bonding region and the tails (Chemistry)
3. most electrons (core) are "irrelevant"
4. relativistic effects
5. tiny but finite nucleus



atomic valence wave functions (s and d) of Pt

Strategies

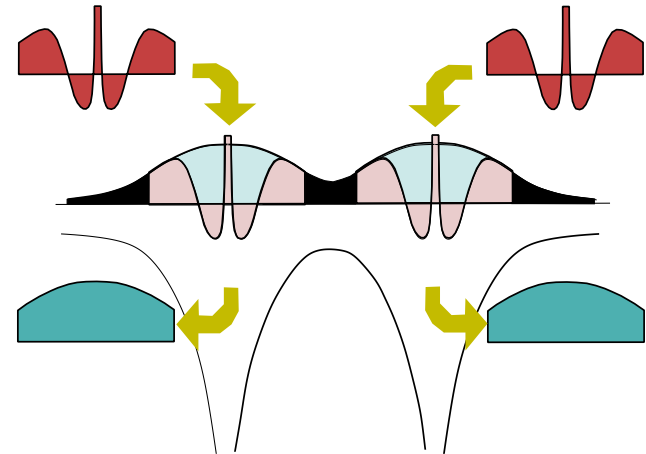
Pseudopotentials



- Chop off singular potential
- node-less wave functions
- no core states
- no information on inner electrons
- transferability problems

Hamann-Bachelet-Schlüter, Kerker,
Kleinman-Bylander, Troullier Martins,
Ultrasoft, etc

Augmented waves



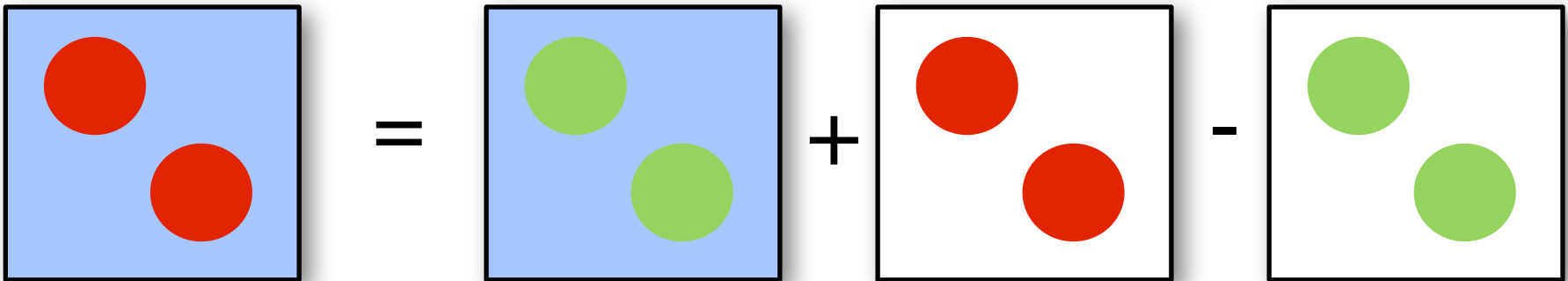
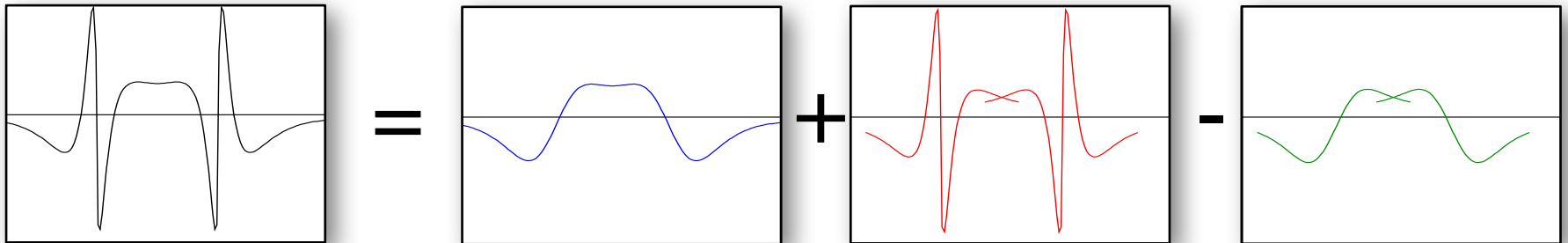
- start with envelope function
- replace incorrect shape with atomic partial waves
- complex basis set
- retain full information on wave functions and potential

LMTO, ASW, LAPW, APW, KKR, PAW,
(all-electron)

PAW augmentation

$$\underbrace{|\psi\rangle}_{\text{all-electron}} = \underbrace{|\tilde{\psi}\rangle}_{\text{pseudo}} + \underbrace{|\psi^1\rangle}_{\text{1-center, all-el.}} - \underbrace{|\tilde{\psi}^1\rangle}_{\sum_{\alpha} |\tilde{\phi}_{\alpha}\rangle \langle \tilde{p}_{\alpha} | \tilde{\psi}\rangle}$$

$\sum_{\alpha} |\phi_{\alpha}\rangle \langle \tilde{p}_{\alpha} | \tilde{\psi}\rangle$
1-center, pseudo



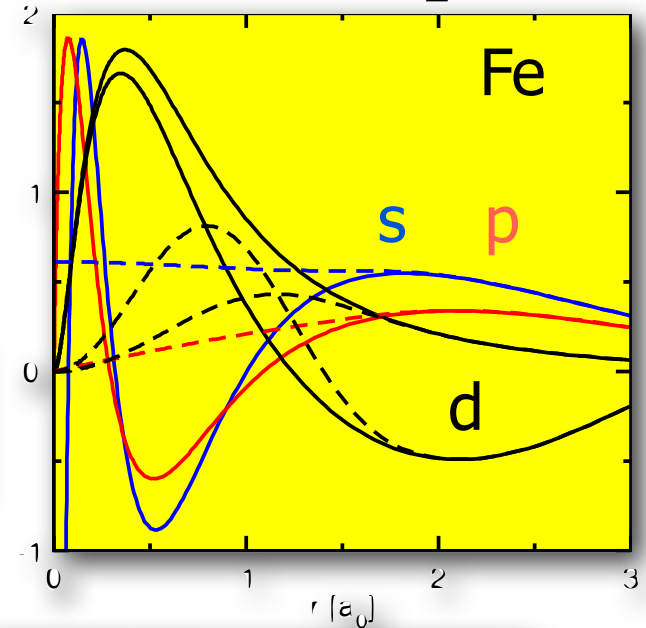
PAW transformation theory

$$\underbrace{|\psi\rangle}_{\text{all-electron true}} = \hat{\mathcal{T}} \underbrace{|\tilde{\psi}\rangle}_{\text{pseudo auxiliary}}$$

$$\hat{\mathcal{T}} = \hat{1} + \sum_R \hat{S}_R$$

with

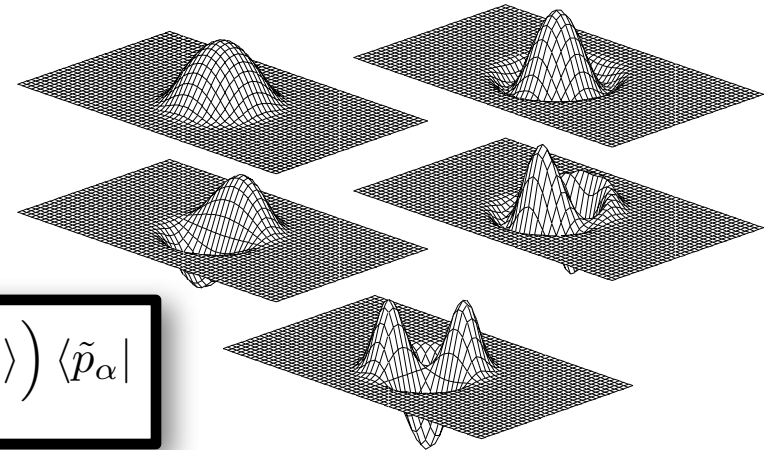
$$\hat{S}_R = \sum_{\alpha} (|\phi_{\alpha}\rangle - |\tilde{\phi}_{\alpha}\rangle) \langle \tilde{p}_{\alpha}|$$



$$|\psi\rangle = \underbrace{|\tilde{\psi}\rangle}_{\text{plane waves}} + \sum_{\alpha} \left(\underbrace{|\phi_{\alpha}\rangle}_{\text{atomic partial wave}} - \underbrace{|\tilde{\phi}_{\alpha}\rangle}_{\text{auxiliary partial wave}} \right) \underbrace{\langle \tilde{p}_{\alpha} | \tilde{\psi} \rangle}_{\text{projector function}}$$

PAW transformation theory

all-electron		pseudo
$ \psi\rangle$	$= \hat{T}$	$ \tilde{\psi}\rangle$
true		auxiliary



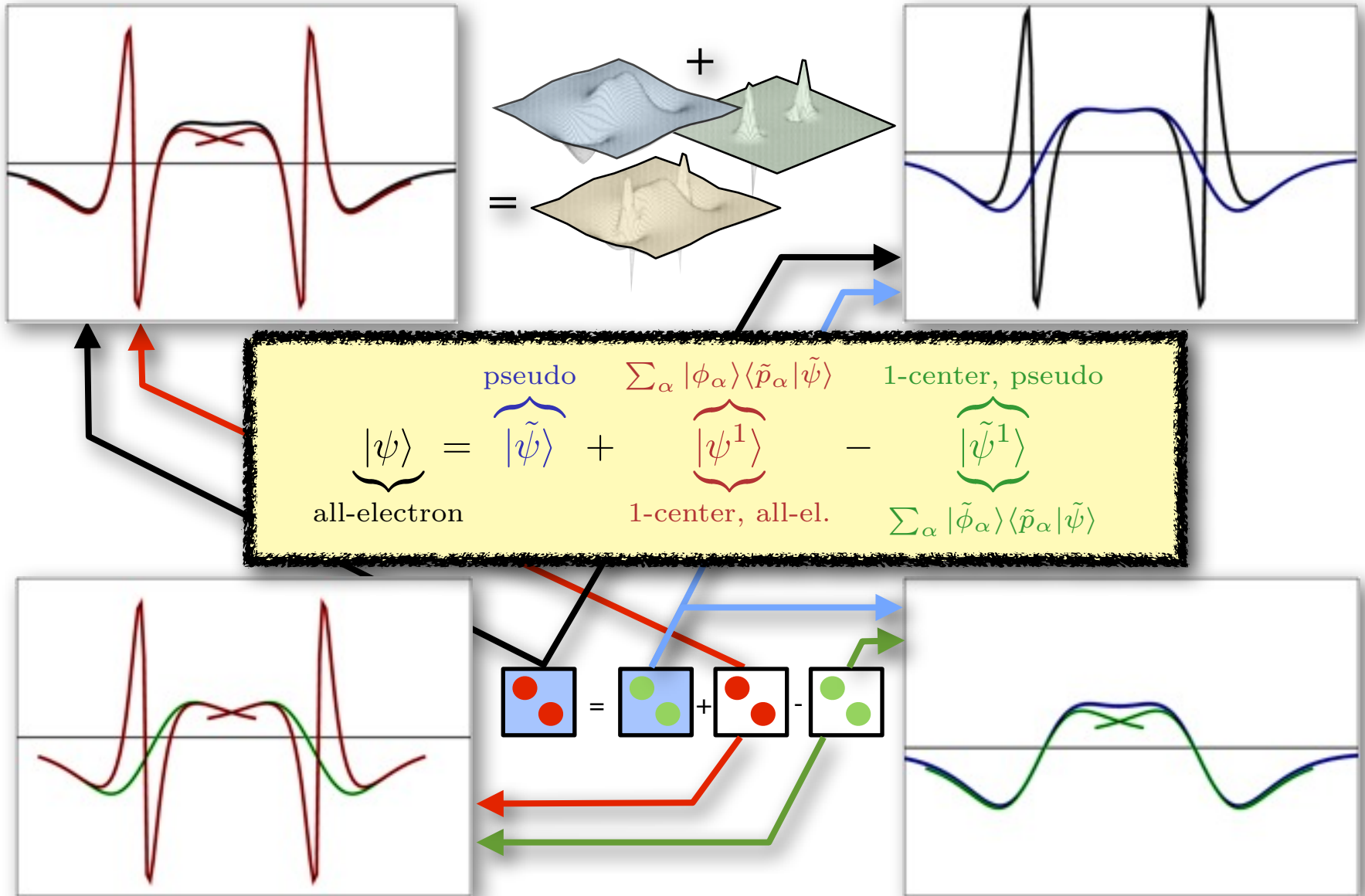
$$\hat{T} = \hat{1} + \sum_R \hat{S}_R$$

with

$$\hat{S}_R = \sum_{\alpha} (|\phi_{\alpha}\rangle - |\tilde{\phi}_{\alpha}\rangle) \langle \tilde{p}_{\alpha}|$$

$$|\psi\rangle = \underbrace{|\tilde{\psi}\rangle}_{\text{plane waves}} + \sum_{\alpha} \left(\underbrace{|\phi_{\alpha}\rangle}_{\text{atomic partial wave}} - \underbrace{|\tilde{\phi}_{\alpha}\rangle}_{\text{auxiliary partial wave}} \right) \underbrace{\langle \tilde{p}_{\alpha} | \tilde{\psi} \rangle}_{\text{projector function}} \underbrace{|\tilde{\psi}\rangle}_{\text{plane waves}}$$

PAW augmentation



PAW total energy

Also, the total energy is written as sum of

- an extended plane wave part
- two one-center expansions for each site

$$E'[\{|\tilde{\psi}_n\rangle, R_j\}] = \tilde{E} + \sum_R (E_R^1 - \tilde{E}_R^1)$$

$$\begin{aligned} \tilde{E} &= \sum_n \langle \tilde{\Psi}_n | \frac{-\hbar^2}{2m_e} \nabla^2 | \tilde{\Psi}_n \rangle + \int d^3r \bar{v}(\vec{r}) \tilde{n}(\vec{r}) \\ &+ \frac{1}{2} \int d^3r \int d^3r' \frac{e^2 [\tilde{n}(\vec{r}) + \tilde{Z}(\vec{r})] [\tilde{n}(\vec{r}') + \tilde{Z}(\vec{r}')] }{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} + E_{xc}[\tilde{n}(\vec{r})] \end{aligned}$$

$$\begin{aligned} E_R^1 &= \sum_{i,j \in R} D_{i,j} \langle \phi_j | \frac{-\hbar^2}{2m_e} \nabla^2 | \phi_i \rangle + \sum_{n \in R} \langle \phi_n^c | \frac{-\hbar^2}{2m_e} \nabla^2 | \phi_n^c \rangle \\ &+ \frac{1}{2} \int d^3r \int d^3r' \frac{e^2 [n^1(\vec{r}) + Z(\vec{r})] [n^1(\vec{r}') + Z(\vec{r}')] }{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} + E_{xc}[n^1(\vec{r})] \end{aligned}$$

$$\begin{aligned} \tilde{E}_R^1 &= \sum_{i,j \in R} D_{i,j} \langle \tilde{\phi}_j | \frac{-\hbar^2}{2m_e} \nabla^2 | \tilde{\phi}_i \rangle + \int d^3r \bar{v}(\vec{r}) \tilde{n}^1(\vec{r}) \\ &+ \frac{1}{2} \int d^3r \int d^3r' \frac{e^2 [\tilde{n}^1(\vec{r}) + \tilde{Z}(\vec{r})] [\tilde{n}^1(\vec{r}') + \tilde{Z}(\vec{r}')] }{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} + E_{xc}[\tilde{n}^1(\vec{r})] \end{aligned}$$

Compensation density:

"smart zero"

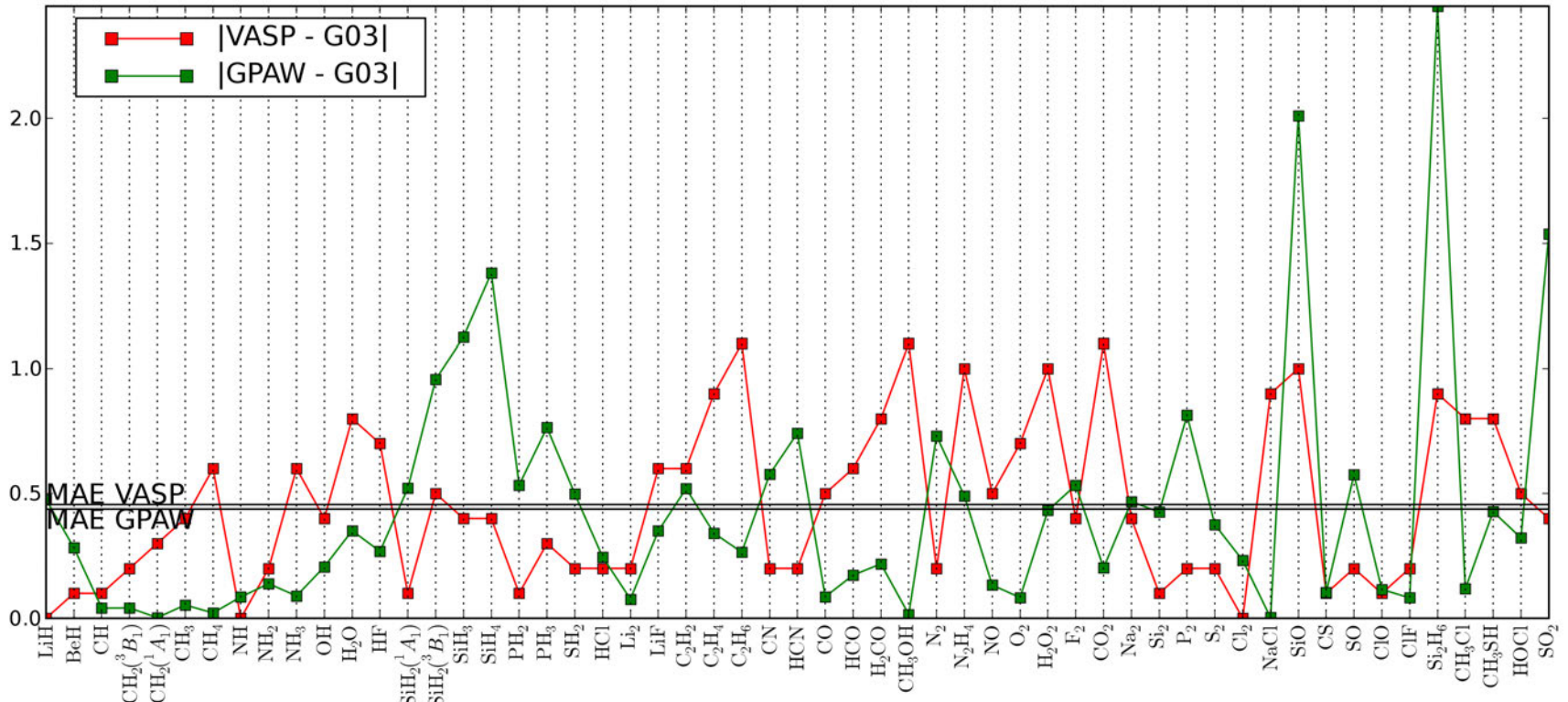
contains pseudized core
(non-linear core correction)

Accuracy

- VASP: [Paier,Hirschl, Marsman, Kresse JCP122,234102 (1005)]
- GPAW: [Carsten Rostgaard]

PBE atomization energies relative to Gaussian:

Atomization energy error in kcal/mol



The End